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The fractionation of nickel between olivine and augite as a geothermometer

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Abstract—The coexisting olivine, clinopyroxene and glass of five samples collected from the Makaopuhi lava lake in Hawaii, at temperatures ranging from 1050 to 1160°C were analysed for nickel with an electron probe microanalyser. The results strongly suggest that the distribution of nickel between these three phase pairs well obeys the thermodynamic partition law, and that under favourable conditions, the distribution coefficients permit the estimation of the crystallisation temperature within an accuracy of 10–20°C.

It is concluded that the application of the Makaopuhi data to plutonic and to other volcanic rocks should be carried out with caution because the effect of pressure and the changing composition of the phases upon the numerical values of the distribution coefficients is not known quantitatively.

INTRODUCTION

THE use of partition coefficients for appropriate trace elements as geologic thermometers is attracting increasing interest, and the subject has been recently discussed by various authors (BARTH, 1961; BETHKE *et al.*, 1958; BETHKE and BARTON, 1959; McINTIRE, 1963; HÄKLI, 1963). Apart from BARTH's study which employed the distribution of Na, Ca, Sr and Ba between acid plagioclase and alkali feldspar as a temperature indicator, relatively little has been published about the applications of this method to geological problems.

The thermodynamics underlying the method is simple and can be reviewed briefly as follows. The chemical potential μ of a component distributed between two phases I and II is in phase I

$$\mu_I = \mu_I{}^0 + RT \ln a_I$$

and in phase II

$$\mu_{II} = \mu_{II}{}^0 + RT \ln a_{II}$$

where a_I and a_{II} are the activities of the component in two phases, μ_I and μ_{II} are the chemical potentials of the component in phase I and II, respectively, R is the gas constant, and T the absolute temperature. At equilibrium the two values of the potential are equal and since $\mu_I{}^0$ and $\mu_{II}{}^0$ are constants, at fixed temperature and pressure, it follows that

$$a_I/a_{II} = \text{constant } (k)$$

If the concentration of the element in both phases is low, both solutions will obey Henry's law (i.e. that activity/concentration = constant) and therefore the ratio of activities in the equation above may be replaced by the ratio of concentrations.

In a general case the numerical value of a partition coefficient is not constant but depends on temperature, pressure and composition of the phases. Holding pressure and composition constant and assuming ΔH to be independent of temperature, pressure and composition, the dependence of the partition coefficient on temperature can be written

$$\ln k = - \Delta H/RT + B$$

where ΔH is enthalpy (the difference between the heats of solution of the trace component in phase I and phase II, respectively) and B is an integration constant.

For the above relation to be generally valid the compositions of the phases between which the trace component is distributed must stay, at least approximately, unchanged during crystallization. Otherwise the chemical potential of the trace component may change, due to the changing bulk composition of the phases, and thus alter the numerical value of the partition coefficient. This variation may be wrongly attributed to the change in temperature or pressure. Several other require-
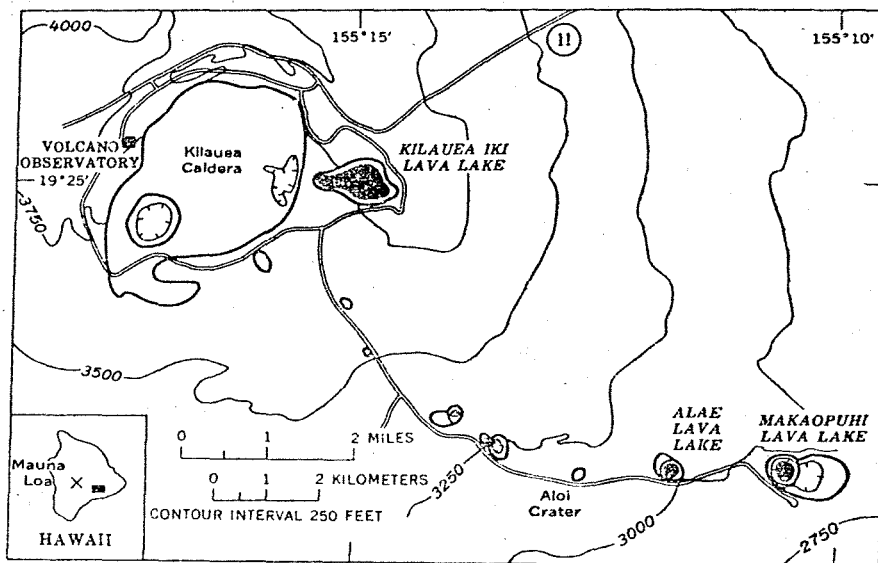

Fig. 1. Map of the Kilauea Volcano area showing the location of the Makaopuhi lava lake.

ments must also be fulfilled before the partition coefficients can be successfully used as reliable thermometers. They have been thoroughly discussed by McINTIRE (1963).

This paper reports the distribution of nickel among olivine, augite and glass as a function of temperatures. Nickel was chosen as a trace element for two reasons: (1) nickel has an affinity for the earliest minerals to crystallize, with the result that its distribution is sensitive to temperature over a wide range of liquidus temperatures; (2) the determinations of even a low nickel concentration can be carried out conveniently and with sufficient accuracy using an electron probe microanalyser. The dependence of the distribution coefficient on temperature was determined using the material collected from Makaopuhi lava lake in Hawaii.

MAKAOPUHI LAVA LAKE: GEOLOGIC AND PETROLOGIC SETTING,
SAMPLING TECHNIQUES, AND MEASUREMENT OF TEMPERATURES

During 5–15 March 1965 an eruption on the upper east rift zone of Kilauea Volcano, Hawaii, poured about 7,300,000 m^3 of tholeiitic basalt into Makaopuhi pit crater (Fig. 1, OKAMURA et al., 1966). After drainback of 2,300,000 m^3 a pond of lava 83 m thick was left in the crater. The erupted lava was quite uniform in bulk composition. Analyses of three samples of pumice collected during the eruption are given in Table 1. During and following the eruption, staff members of the U.S. Geological

Table 1. Chemical analyses of pumice from the
eruption into Makaopuhi Pit Crater

Sample no. Oxide	M-1	M-20	M-26
SiO_2	50·19	50·13	50·06
Al_2O_3	13·46	13·26	13·19
Fe_2O_3	1·39	1·38	1·47
FeO	9·88	9·88	9·81
MgO	8·34	8·33	8·49
CaO	10·81	10·83	10·73
Na_2O	2·34	2·30	2·28
K_2O	0·55	0·54	0·53
H_2O^+	0·11	0·10	0·17
H_2O^-	0·00	0·01	0·00
TiO_2	2·59	2·68	2·62
P_2O_5	0·27	0·27	0·27
MnO	0·17	0·17	0·17
CO_2	0·01	0·01	0·01
Cl	0·02	0·03	0·02
F	0·04	0·04	0·04
Subtotal	100·17	99·96	99·86
less O	0·02	0·03	0·02
Total	100·15	99·93	99·84

M-1. Pumice collected 5 March 1965 at Makaopuhi Crater.

M-20. Pumice collected 14 March 1965 at Makaopuhi Crater.

M-26. Pumice collected 15 March 1965 at Makaopuhi Crater.

Chemical analyses done in the Denver Rock analysis laboratory of the U.S. Geological Survey under the direction of LEE C. PECK using methods outlined in L. C. PECK, 1964 (analyst: G. O. Riddle).

Survey's Hawaiian Volcano Observatory obtained samples of crust and melt, measured temperature gradients in the crust and the melt, and traced the growth of the crust through time.

Temperature was measured using Cr–Al and Pt–PtRh$_{10}$ thermocouples. A maximum temperature of 1160°C was measured during the eruption in a small pahoehoe flow near the edge of the rising lava lake. Later, thermocouples were used

in both cased and uncased drill holes, and some of the cased holes were extended into the melt. The highest temperature measured in a drill hole was 1140°C.

Samples of lava were obtained in three ways. Lava at the edge of the rising lake was collected in hollow alumina tubes. Solidified and partially molten crust at temperatures below 1075°C was collected by ordinary methods of core-drilling. (See PECK et al., 1964, for description of drilling procedures.) Melt at temperatures above 1075°C was collected in hollow alumina tubes pushed through the bottom of stainless steel casings which were emplaced by pushing to the desired depth in the melt.

Modal data were obtained for all samples in which interstitial glass was present. Because of the presence of drilling water, meaningful temperatures could not be measured at the time most samples were collected. The isotherms, however, are found to move downward in the lake proportionally to the square root of time and hence a profile for any drilling date can be obtained by extrapolation forward or backward in time of temperatures obtained either before or after drilling when effects of drilling water are not present. An illustrated discussion of temperature assignment is given in PECK et al. (1964), for Alae lava lake and the same discussion applies to Makaopuhi lava lake. The modal percent glass can be plotted against the temperature range of collection. From the generalized temperature–volume per cent glass curve, temperature of any sample can be assigned with an accuracy of ±10°C. Combining temperature data with modal determination of mineral percentages a paragenesis can be worked out as shown in Table 2.

Table 2. Sequence of crystallization in Makaopuhi lava lake

Mineral	Temperature of first appearance (°C)	Volume % glass
Olivine	ca. 1200	100
Clinopyroxene	ca. 1180	96
Plagioclase	1160 ± 10	91
Opaques (magnetite and ilmenite)	1070 ± 10	43
Apatite	1020 ± 10	11
Solidus	990 ± 10	3
		(residual glass)

PARTITIONING OF NICKEL; ANALYTICAL TECHNIQUES AND RESULTS

Five samples were used to study the distribution of nickel among olivine, clinopyroxene, and the liquid (glass). Temperatures and modal data for these samples are shown in Table 3. The compositions of olivines and pyroxenes vary with temperature and especially the larger grains show a distinct zoning, whereas the small crystals are often relatively homogeneous and thus suitable for electron probe analysis.

The main components of olivines were determined using a chemically analysed olivine crystal as a standard. For pyroxene analyses a diopside standard was employed for determinations of Ca, Mg and Fe, and an alkali feldspar standard was used for determination of Na. A quartz crystal was used as a standard for Si. The intensities were corrected for matrix absorption and matrix enhancement as described

by BIRKS (1963) and THEISEN (1965). The analyses were carried out with a Geoscan microanalyser. Partial electron probe analyses of 5 olivines and pyroxenes are compiled in Table 4 along with partial analyses of the coexisting glass.

For the nickel determinations an olivine crystal of gem quality containing 2840 ppm Ni was used as a standard. Olivine and clinopyroxene grains were chosen

Table 3. Modal analyses of samples from Makaopuhi lava lake

Sample No. Type of sample	M-12 Melt coll. in Al_2O_3 tube	M 21-26 Melt coll. in Al_2O_3	M 7-7 Drill core	M 1-6 Drill core	M 5-13 Drill core
Temperature of collection	1160°	1120°	1075°	1070°	1050°
Constituents (vol. %)					
Olivine	3·1	2·8	4·2	1·4	1·6
Clinopyroxene	6·2	13·6	32·3	35·7	45·4
Plagioclase	0·5	7·9	19·6	20·1	29·4
Opaque	—	—	—	1·1	5·5
Glass	88·2	58·8	34·9	38·4	18·1
Quench*	2·0	16·9	9·0	3·3	—
No of points on 0·3 × 0·3 mm grid	5480	2000	1850	1500	1500

* Oxidation and devitrification products of glass formed during quenching.

Table 4. Partial electron-probe analyses for the Makaopuhi olivines, pyroxenes and glasses

Spec. No. Temp. (°C) Mineral	M-12 1160 Olivine	M 21-26 1120 Olivine	M 7-7 1075 Olivine	M-12 1160 Clin. pyr.	M 7-7 1075 Clin. pyr.	M-12 1160 Glass[3]	M 21-26 1120 Glass[3]	M 7-7 1075 Glass[3]	M 1-6 1070 Glass[3]	M 5-13 1050 Glass[3]
SiO_2	38·7[1]	38·3[1]	37·2[1]	51·0[1]	51·0	51·2	50·5	50·0	51·8	55·7
Al_2O_3	—	—	—	3·40	3·40	—	—	—	—	—
TiO_2	—	—	—	1·37	1·2	—	—	—	—	—
FeO^2	21·05	25·20	30·42	8·87	8·20	11·4	13·4	13·9	16·1	14·6
MgO	39·24	36·60	32·17	14·90	15·8	8·2	6·3	4·0	4·2	1·9
CaO	0·99	0·36	0·34	19·73	19·0	—	—	—	—	—
MnO	0·19	0·19	0·28	0·10	0·12	—	—	—	—	—
Na_2O	—	—	—	0·30	0·4	—	—	—	—	—
	100·17	100·65	100·41	99·67	99·12	70·8	70·2	67·9	72·1	72·2

[1] SiO_2 equivalent calculated from Ca, Mg and Fe.
[2] Total iron as FeO.
[3] Absoute values are approximate as complete analyses were not made. Relative values are accurate to ±0·3%.

whose diameters were from 10 to 20 μ. Larger crystals were not used because it was noticed that they were not always at chemical equilibrium with the melt. Due to the small grain size the polished thin sections had to be made as thin as the normal microscopic slides, i.e. 0·03 mm. Before the analyses the polished thin sections were coated with aluminum.

To increase the intensity of the NiK_α line as much as possible a working voltage of 40 kV was used. The use of a high voltage source was advantageous because nickel occurs as a heavy element in a light matrix. An increased voltage results in an increased peak to background ratio which increases the precision of determination

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for small amounts of nickel. The intensity of the background was measured at a distance of two degrees from the NiK$_\alpha$ line on both sides of the peak.

At least ten determinations were done for each mineral phase in every sample; one spot was analysed on each grain. Due to the slight variation in Ni-content from one grain to another it was established that the most reliable results were obtained if, instead of counting the NiK$_\alpha$ impulses from a few grains for a long time, many crystals were analysed using relatively short counting times.

The nickel concentrations of olivines, clinopyroxenes and glasses are compiled in Table 5. The values are averages of about ten determinations each and they are estimated to be correct within ±5 ppm.

Table 5. The nickel concentrations of coexisting olivines, clinopyroxenes and glasses in the Makaopuhi lava lake. Electron-probe analyses. 40 kV, 0·6 μA, LiF-crystal.

Sample	Temperature °C	Ol^{Ni} ppm	Py^{Ni} ppm	Gl^{Ni} ppm	Ol^{Ni}/Gl^{Ni}	Py^{Ni}/Gl^{Ni}	Ol^{Ni}/Py^{Ni}
M-12	1160	1555	255	115	13·5	2·22	6·10
M 21-26	1120	1310	245	87	15·1	2·82	5·35
M 7-7	1075	955	240	60	15·9	4·00	3·98
M 1-6	1070	935	235	57	16·4	4·12	3·98
M 5-13	1050	840	220	50	16·8	4·40	3·82

The partition coefficients between olivine and glass, clinopyroxene and glass, and olivine and clinopyroxene were computed and are also summarized in Table 5. The logarithms of the partition coefficients are plotted against the inverse of the absolute temperature in Fig. 2. The straight lines obtained indicate that the fractionation of nickel among these three phases obeys the thermodynamic distribution law within limits of analytical accuracy.

The lines in Fig. 2 permit the computation of ΔH and B for the three pairs of phases; these are shown in Table 6. However, due to the low number of analyses the values presented in Table 6 must be considered only as first approximations needing revision whenever more information becomes available.

It is of interest to notice that with the falling temperature relatively more nickel enters into the lattice of olivine and pyroxene from the melt. As indicated by the numerical values of ΔH this tendency is stronger for pyroxene than for olivine, and consequently, the ratio Ol^{Ni}/Py^{Ni} tends to decrease with falling temperature.

The slopes of the three lines are rather steep making the coefficients fairly suitable for the determination of temperature. In practice the distribution coefficients $k = Ol^{Ni}/Gl^{Ni}$ and $k = Py^{Ni}/Gl^{Ni}$ have a limited direct application to geothermometry due to the scarcity of the glass phase in nature. However, if the nickel content of the groundmass of a porphyritic rock can be measured, either directly or from analyses of the whole rock and the phenocrysts, then it may be possible to derive the temperature at which the rock was quenched.

A distribution coefficient which has a straightforward application to geothermometry is $k = Ol^{Ni}/Py^{Ni}$. The slope of the line is sufficiently steep and, as the Makaopuhi data indicate, under favourable conditions it permits the temperature to be estimated with an accuracy of about 10–20°C.
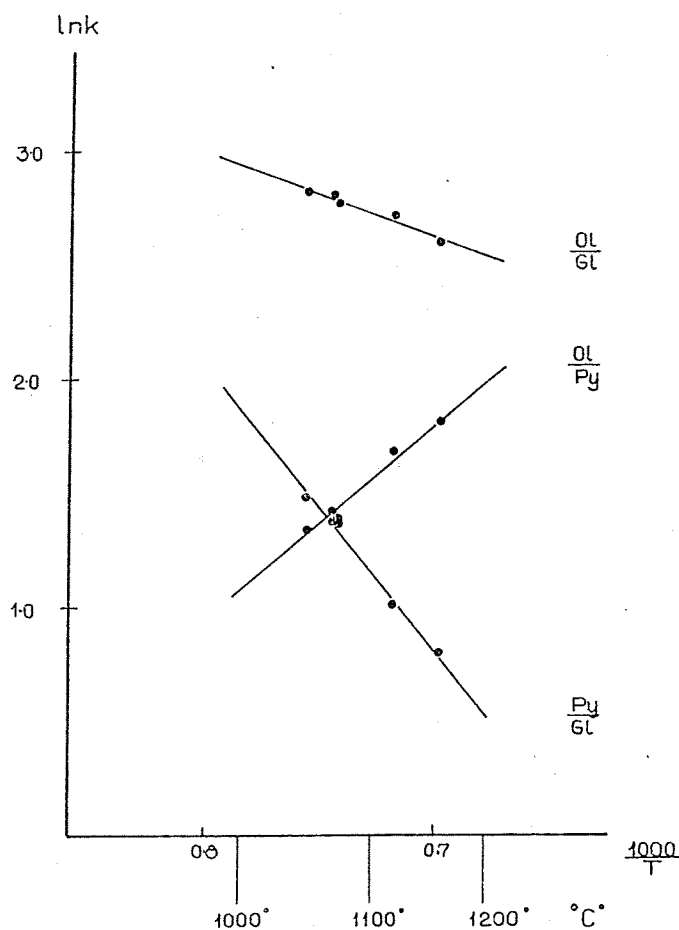
Fig. 2. Relation between temperature and the numerical values of the Ni-distribution coefficients for the mineral pairs: olivine–glass, clinopyroxene–glass and olivine–clinopyroxene in the Makaopuhi lava lake. Abscissa: the inverse of the absolute temperature. Ordinate: natural logarithms to the distribution coefficients.

Table 6. The values of ΔH and B for the three phase pairs of the Makaopuhi lava lake

	ΔH (cal/mole)	B
Ol^{Ni}/Gl^{Ni}	$-7\cdot400$	$0\cdot03$
Py^{Ni}/Gl^{Ni}	$-24\cdot800$	$-7\cdot85$
Ol^{Ni}/Py^{Ni}	$16\cdot800$	$7\cdot65$

In conclusion it should be emphasized that the use of the distribution coefficients plotted in Fig. 2 to obtain temperatures of crystallization for other rocks is limited by two factors. First, we do not know the quantitative effects of changing total pressure, water pressure and chemical activities such as SiO_2 and FeO on the distribution coefficients. Until these are known it is not possible to derive from the data

for Makaopuhi absolute temperatures of some other rocks for which nickel in olivine, pyroxene, or glass, have been determined. It is probable, however, that relative values of the distribution coefficients for any one genetically related suite of rocks predominantly reflect differences in crystallization temperatures, although effects of other parameters will inevitably be present. Secondly it must be kept in mind that the temperature determined from a distribution coefficient is the temperature below which the nickel component was no longer mobile or free to diffuse among the various phases of the rock. Usually this will represent the solidification temperature or in the case of volcanic rocks, the temperature at which the rock was erupted and quenched. Any rocks for which either subsolidus re-equilibration occurred or for which nickel has been added or removed metasomatically, will not yield temperatures representative of the original (liquidus) crystallization.

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